

What is claimed is:

1. A method for determining the quantity of both brightener and leveler in an electroplating bath comprising the steps of:

a) determining the amount of brightener by a method selected from cyclic voltammetric stripping and cyclic pulse voltammetric stripping;

b) obtaining a plurality of plating baths where each bath has a known and different quantity of said brightener and leveler, but where the quantity of each in each bath differs from the quantity in the other baths;

c) for each bath, providing a counter electrode, a cleaned working electrode and a reference electrode immersed in said bath, and carrying out a predetermined sequence of steps comprising:

1. cleaning and oxidizing the surface of the working electrode at a fixed potential for a period of time;

2. equilibrating said working electrode to absorb brightener according to a step selected from equilibrating without energy input for a time until the change in energy output with time is minimal and equilibrating for a set time at a fixed potential;

3. plating metal ions on said working electrode with energy input for a time sufficient to measure initial plating energy output; and

4. optionally continuing to plate metal ions for a time sufficient to measure the change in energy output with time;

5. stripping at a potential and for a period of time sufficient to remove the metal ions plated in steps 3 and 4;

d) for each bath, correlating the quantity of leveler with the energy output value obtained in step 3 or 4;

e) obtaining a plating bath having an unknown quantity of brightener and leveler, placing said electrodes in said bath and performing said predetermined sequence of steps;

f) choosing from said correlations in step d), a particular correlation for a bath containing substantially the amount of brightener determined in step a); and

g) choosing from the particular correlation in step f), a quantity of leveler which corresponds to said energy outputs recorded for said bath with the unknown quantity of brightener and leveler.

2. The method of claim 1 wherein the electroplating bath is a copper electroplating bath.

3. The method of claim 1 wherein the working electrode is a platinum electrode.

4. The method of claim 1 wherein the electrode is a rotating disk electrode.

5. A method for determining the quantity of both brightener and leveler in an electroplating bath comprising the steps of:

a) obtaining a plurality of plating baths, where each bath has a known and different quantity of said brightener and leveler, but where the quantity of each in each bath differs from the quantity in the other baths;

b) sweeping for each of said baths an inert, working electrode at a predetermined rate through a plurality of voltammetric cycles until a condition of steady state is obtained, each of said voltammetric cycles including a metal plating range and a metal stripping range for each of said baths of said plurality of baths, each of said voltammetric cycles comprising a sweeping of a voltage toward one polarity followed by a sweeping of said voltage toward a reverse of said one polarity to complete said cycle;

c) measuring the coulombs utilized during said metal stripping range of said cycle for each of said baths of said plurality of baths, whereby a correlation is obtained between the effective quantity of brightener and said coulombs utilized during said metal stripping range;

d) obtaining a bath having an unknown quantity of both brightener and leveler;

e) sweeping for said unknown bath an inert, working electrode at said predetermined rate through a plurality of voltammetric cycles until a condition of steady state is obtained, each of said voltammetric cycles including a metal plating range and a

metal stripping range for said bath having an unknown quantity of brightener, each of said voltammetric cycles comprising a sweeping of a voltage toward one polarity followed by a sweeping of said voltage toward a reverse of said one polarity to complete said cycle;

f) measuring the coulombs utilized during said metal stripping range of said cycle for said bath having an unknown quantity of brightener;

g) choosing from said correlation a quantity of brightener which corresponds to said coulombs utilized for said bath having an unknown quantity of organic leveling agent;

h) for each of said plurality of plating baths in step a), providing a counter electrode, a cleaned working electrode and a reference electrode immersed in said bath, and carrying out a predetermined sequence of steps comprising:

1. cleaning and oxidizing the surface of the working electrode at a fixed potential for a period of time;
2. equilibrating said working electrode to absorb brightener according to a step selected from equilibrating without energy input for a time until the change in energy output with time is minimal and equilibrating for a set time at a fixed potential;
3. plating metal ions on said working electrode with energy input for a time sufficient to measure initial plating energy output; and
4. optionally continuing to plate metal ions for a time sufficient to measure the change in energy output with time;
5. stripping at a potential and for a period of time sufficient to remove the metal ions plated in steps 3 and 4;

i) for each bath, correlating the quantity of leveler with the energy output value obtained in step 3 or 4;

j) obtaining a plating bath having an unknown quantity of brightener and leveler, placing said electrodes in said bath and performing said predetermined sequence of steps;

k) choosing from said correlations in step i), a particular correlation for a bath containing substantially the amount of brightener determined in step g); and

l) choosing from the particular correlation in step k), a quantity of leveler which corresponds to said energy outputs recorded for said bath with the unknown quantity of brightener and leveler.

6. The method of claim 5 wherein the electroplating bath is a copper electroplating bath.

7. The method of claim 5 wherein the working electrode is a platinum electrode.

8. The method of claim 5 wherein the electrode is a rotating disk electrode.

9. A method for determining the quantity of leveler in an electroplating bath comprising the steps of:

a) obtaining a plurality of plating baths where each bath has a known and different quantity of brightener and leveler, wherein the quantity of leveler in each bath differs from the quantity in the other baths;

b) for each bath, providing a counter electrode, a cleaned working electrode and a reference electrode immersed in said bath, and carrying out a predetermined sequence of steps comprising:

1. cleaning and oxidizing the surface of the working electrode at a fixed potential for a period of time;

2. equilibrating said working electrode to absorb brightener according to a step selected from equilibrating without energy input for a time until the change in energy output with time is minimal and equilibrating for a set time at a fixed potential;

3. plating metal ions on said working electrode with energy input for a time sufficient to measure initial plating energy output; and

4. optionally continuing to plate metal ions for a time sufficient to measure the change in energy output with time;

5. stripping at a potential and for a period of time sufficient to remove the metal ions plated in steps 3 and 4;

c) for each bath, correlating the quantity of leveler with the energy output value obtained in step 3 or 4;

d) obtaining a plating bath having an unknown quantity of leveler;

e) diluting the bath having an unknown quantity of leveler with a leveler-free composition comprising a fixed concentration of brightener and placing said electrodes in said bath and performing said predetermined sequence of steps;

f) choosing from said correlation in step c), a quantity of leveler which corresponds to said energy outputs recorded for said bath with the unknown quantity of leveler.

10. The method of claim 9 wherein the electroplating bath is a copper electroplating bath.

11. The method of claim 9 wherein the working electrode is a platinum electrode.

12. The method of claim 9 wherein the electrode is a rotating disk electrode.